Structure and Packing Density of Liquid Metals

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Recent results concerning the structure of microparacrystals established in different melts are reported. In spite of structural differences among the investigated samples the reduced density is always the same. This approach is possibly a first step towards a correlation between the hard sphere concept of statistical mechanics and our refined structural analysis.

The diffraction pattern of molten metals shows several intensity-maxima, which can be interpreted in a similar way as the Debye-Scherrer pattern of crystalline powders. For this purpose, however, it is necessary to introduce liquid-like distortions. Such an approach has been given by the concept of paracrystallinity [1], which contains the well known equations of crystallography [2] as limiting case. Kratky [3, 4] was the first who tried to construct the pair correlation function by randomly oriented distorted microdomains. Satisfying results have recently been obtained in the case of fcc- and bcc-molten metals by means of convolution polynomials [5, 6]. In a paracrystal, the positions of atoms are labeled by integers i, k, l and p, q, r, corresponding to positions on lines, rows, and columns. The p, q, r are the relative coordinates of an ideal lattice site. However, contrary to the crystalline state, the distance statistics of pairs (i, k, l) and $(i+p, k+q, l+r)$, averaged over all i, k, l, become broader with increasing $(|p|, |q|, |r|)$. The average over many paracrystals with arbitrary orientations results in spherical shells. Apart from some well known factors and additive terms these result in the pair correlation function.

Instead of simply averaging over all i, k, l, one can first rotate the different paracrystals until they are aligned in parallel to each other and then average over all these oriented (i, k, l) environments.

The resulting correlation function is no longer spherically symmetric, but is splitted into individual density humps $W_{pqr}(\underline{x})$ whose centers form a three-dimensional lattice. In some (i, k, l) environments a site (p, q, r) may be vacant, in others doubly occupied. Thus $\int W_{pqr}(\underline{x})\,\mathrm{d}\underline{x}$ is not necessarily unity. The average distance of nearest neighbours is given by

$$\frac{1}{K_1}\int \Sigma\,|\underline{x}|\,W_{pqr}(\underline{x})\,\mathrm{d}\underline{x} = r_1 .$$

The summation is performed over all p, q, r with

$$p^2+q^2+r^2 = \min > 0 .$$

For the same p, q, r, the coordination number K_1, i.e. the average number of nearest neighbours is defined by

$$K_1 = \int \Sigma\, W_{pqr}(\underline{x})\,\mathrm{d}\underline{x}; \quad p^2+q^2+r^2 = \min > 0 .$$

If Schottky and Frenkel defects are created on melting, K_1 is found to be smaller than the corresponding number for the crystalline state. K_1 may be larger, however, if interstitials are created.

The paracrystalline model uses only the nearest neighbour statistics to calculate approximately the whole three-dimensional correlation function by a three-dimensional polynominal. The rotational average of this function can be compared with experimental pair correlation functions. If the agreement is good, one can conclude that the paracrystalline nearest neighbour distribution is a good approximation for the real one, so that the paracrystalline coordination number K_{PC} and the corresponding distance r_{PC} should also be good approximations.

The validity of this conclusion is confirmed by the agreement of the other features of the paracrystalline nearest neighbours distributions with data from molecular dynamics calculations of molten salts [7]. There the preferential structure of the melt has been directly calculated. It might be identified with a paracrystalline distorted surrounding.

The aim of this paper is to present new results concerning the reduced densities of several molten

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metals and compare them with conventional theories of liquids. Detailed informations regarding the fundamental ideas of the model of paracrystals are reported elsewhere [7 – 10]. It was found that molten Pb has a paracrystalline fcc short range order [5], while melts of Li, Na, K and Rb have bcc short range order [6]. Therefore, in the following we will talk of "fcc melts" and "bcc melts". The fcc-melts have a coordination number $K_{\mathrm{PC}} \approx 11.5$ and a mean distance r_{PC} between neighbouring atoms equal to the one below the melting point, i. e. r_{C}. bcc-melts have $K_{\mathrm{PC}} \approx 8.3$ and an r_{PC} value which is a few percent larger than r_{C} (Table 1). The reduced density of the PC-lattice is defined as

$$\eta_{\mathrm{PC}} = \varrho_0 \, r_{\mathrm{PC}}^3 \tag{1}$$

with ϱ_0 the number density of atoms. For crystals, η_{C} equals 1, 1.41 and 1.30 for primitive cubic, fcc- and bcc-lattice cells, respectively. The η_{PC}-data of melts with the corresponding η_{C}-data are shown in Table 1.

Interestingly all the melts under investigation have almost the same η_{PC} value, irrespective of the type of the paracrystalline lattice. Within the experimental errors a constant value $\eta_{\mathrm{PC}} \approx 1.35$ was found. This is almost the average of the η_{C} values of the crystalline fcc- and bcc-lattices and can be explained by vacancies in fcc-melts and interstitials in bcc-melts.

Without considering the structure, Ruppersberg [11] found a striking difference between the reduced densities of fcc- and bcc-melts (cf. Table 1). Since he could not obtain information regarding the *mean* distance r_{PC} between the neighbours, he used the *most frequent* distance d given by the position of the maximum of the pair correlation function. His reduced density

$$\eta' = \varrho_0 \, d^3 \tag{2}$$

turned out to be by 15% smaller than 1.41 for melts of the fcc-metals Pb, Ag, Au, Au, etc. and surprisinly somewhat larger than 1.20 for the melts of the bcc-alkali metals. Thus, Ruppersberg was one of the first to provide information regarding the existence of structural differences of "simple" melts.

Table 1. Coordination numbers K_1, mean interatomic distances r and reduced densities η and η' at the melting point. The subscripts C and PC refer to the solid and liquid state, respectively. The data in brackets are derived from analogy with respect to Pb.

		K_{C}	K_{PC}	r_{C}(Å)	r_{PC}(Å)	η_{C}	η_{PC}	η' Ref. [11]
fcc	Pb	12	11.6	3.54	3.55	1.41	1.37	1.20
	Cu		(11.5)	2.61	(2.61)		(1.35)	1.20
	Ag		(11.5)	2.98	(2.98)		(1.37)	1.21
	Au		(11.4)	2.95	(2.95)		(1.33)	1.22
	Al		(11.3)	2.93	(2.93)		(1.33)	1.21
bcc	Li	8	8.7	3.06	3.16	1.30	1.39	1.37
	Na		8.2	3.73	3.79		1.33	1.35
	K		8.4	4.56	4.72		1.35	1.28
	Rb		8.3	4.95	5.08		1.35	1.28
	Cs		8.0	5.31	5.43		1.37	1.25

Sometimes crystallographers regard atoms as hard spheres which are more or less closely packed. In order to obtain the real packing density σ of hard spheres, it is necessary to multiply the reduced density with the reduced volume $\frac{4}{3}\pi\left(\frac{1}{2}\right)^3$ of a sphere with the diameter 1 $\left(\sigma = \frac{\pi}{6}\eta\right)$.

In order to fit the experimentally observed X-ray- and neutron diffraction data of liquids Ashcroft and Lekner [12] neglected structural differences and used the Percus-Yevick-equation for hard spheres. With the help of the so called hard sphere diameters they found a packing density of $\sigma \sim 0.45$, for all liquid melts, i. e., a reduced density of $\eta = 0.86$ instead of the value 1.35 of Table 1. The definition of σ entails that the lower value demands hard sphere diameters which are by

$$1 - \left(\frac{0.86}{1.35}\right)^{1/3} = 14\%$$

smaller than the mean distance r_{PC} between neighbouring atoms.

The strong correlation between the PY-hard sphere diameter r_{HS} and r_{PC} is to be noted. The fact that r_{HS} is smaller than r_{PC} is to be expected supposing that r_{HS} really represents a hard sphere diameter. The magnitude of the difference between r_{HS} and r_{PC}, i. e., 14%, correlates with the relative width of the nearest neighbours distance statistics resulting from paracrystalline analysis, i. e., 12 to 15%. Obviously, the Percus-Yevick-equation leads to conclusions which conform with the results of a direct structural analysis although the validity of the connection between the pair potential and the Ornstein-Zernike direct correlation function used in the Percus-Yevick-theory is somewhat dubious [13].

We recognize that the phenomenon of a constant reduced density gives no evidence of the same "amorphous-like" structure of all melts. Table 1 shows that r_{PC} in the melt is the same as r_C in the crystal for fcc-lattices; r_{PC} is larger than r_C for bcc-melts. The coordination number K_1 on the other hand slightly decreases for fcc in the melt but increases remarkably for bcc at the melting point. This can be easily explained by the produced vacancies in the fcc-case, which cannot affect the nearest neighbour distance r_{PC} because of the closest possible packing. In bcc-lattices, on the other hand, which have not the largest possible packing density, many atoms can migrate to interstitials thereby increasing r_{PC}.

It is somewhat astonishing that two theories with so different starting points come to the same results concerning the reduced density. This gives some hope that it might be possible to combine the advantages of the Percus-Yevick theory, i. e. easy access to thermodynamical and other physical properties, with the advantages of the paracrystalline theory, i. e. high perspicuity with regard to atomic structures and applicability not only to melts but to a variety of distorted structures like polymers [14] and catalysts [15].

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